Contents lists available at ScienceDirect





journal homepage: www.elsevier.com/locate/superlattices



Peculiarities of the dielectric response of natural zeolite composites prepared by using zeolite and silicon powders



S. Ozturk Koc^a, V.I. Orbukh^b, G.M. Eyvazova^b, N.N. Lebedeva^b, B.G. Salamov^{a, c, *}

^a Physics Department, Faculty of Sciences, Gazi University, Besevler 06500 Ankara, Turkey
^b Baku State University, Institute for Physical Problems, Baku, AZ 1148, Azerbaijan
^c Azerbaijan Academy of Science, Institute of Physics, AZ0143 Baku, Azerbaijan

ARTICLE INFO

Article history: Received 15 October 2015 Received in revised form 12 January 2016 Accepted 15 January 2016 Available online 19 January 2016

Keywords: Nanoporous materials Zeolite powder Silicon powder Frequency Dielectric properties Si concentration

ABSTRACT

We present the real and imaginary part of the dielectric permittivity of natural zeolite composites prepared by using zeolite and silicon powders. The dielectric response (DR) dependences on the frequency (3–300 GHz) of electric field and different Si concentrations (5–33%) are non-monotonic and a maximum peak is observed. This peak position is practically independent on the frequency and its maximum is observed in zeolite composites which included 9% of the Si-powder. Also the maximum peak is decreased by about an order of magnitude when frequency increases from 500 Hz to 5 kHz. Addition of the conductive Si-particles to zeolite-powder leads to two opposite effects. Firstly, the movement of electrons in the Si-particles provides increase of DR. Secondly, cations which leaving from zeolite pores can be neutralized by the particles of Si in the intercrystalline-space. Such a peculiar mechanism for recombination of Si electrons and cations from pores leads to a reduction of DR for large silicon concentrations. Due to the fact that the contribution of free carriers in the decreasing of the DR as the frequency increases, it is consistent with the suggestion that the maximum peak decreases with increasing frequency.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Natural-zeolite (NZ) minerals are good sorbents and exhibit the ability to ion exchange due to their strictly defined pore size and internal cavities (≈ 4 Å). Zeolite represents microporous "sponge" with a pore volume of up to 50% of the skeleton. In Azerbaijan, it is found that 14 types of minerals of the zeolite family associate with magmatism. It is known more than 40 types of NZs mineral. Geological feature of zeolite areas gives reason to believe that the territory of Azerbaijan is one of the most promising regions for NZs [1], which are found wide application in many areas.

On the basis of the radiographic and chemical analysis on alumosilicate-zeolite, it is established that the NZ examined by us is affiliated to zeolites of clinoptilolite (Cl) species [2]. Crystalline structure is composed of an alternating negatively charged alumosilica tetetrahedra AlO₄ and SiO₄, which are interconnected by nodes with a pore-nanochannels of two types A

^{*} Corresponding author. Physics Department, Faculty of Sciences, Gazi University, Besevler 06500 Ankara, Turkey. *E-mail address:* bala@gazi.edu.tr (B.G. Salamov).

and B that dimensions 0.6×0.4 nm - (A type) and 0.4×0.4 nm - (B type) [3]. These channels are filled with the extraframework cations that is, Na⁺, K⁺, Mg²⁺, Ca²⁺, which compensate the negative charges of the framework and a large number of molecules of H₂O-water. Water plays an important role in the stability of Cl framework. Since between the oxygen atoms of the skeleton, the positively charged ions and H₂O molecules form hydrogen bonds, it is believed that H₂O molecules leads to an increase [4–7], the mobility of ions in the pores space. It should be noted that infrared spectra are sensitive to change in both the hydrogen and coordination bonds in the crystal. This is resulted in our interest to the measurement of the absorption of water in Cl, where the absorption spectra of NZ-Cl in a wide frequency range from 3600 cm⁻¹–100 cm⁻¹. Identified bands are caused by the absorption of water in the pores of the zeolite. The observed broad band at a frequency of 3470 cm⁻¹ is caused by vibration of water molecules. The strongest band at a frequency of 1631 cm⁻¹ confirms the higher diffusion mobility.

Under various conditions a number of works is devoted to study on dielectric spectra of zeolites. In Ref. [8] revealed that the dependence of dielectric properties of the zeolite is based on the type of the primary ion, i.e. an ion which controlled the ion-ion migration polarization. In this work, we studied the temperature dependence of dielectric permittivity at various frequencies. It is found that the experimental results are satisfactorily described by a model of two-componential zeolite-air pores system. It should be noted that in this work before experiment the water removed by evacuation or annealing from pores of the framework. Influence of water on dielectric properties of zeolites is studied in Ref. [9]. In this study, the NZ Ca-Cl was investigated. It has been studied that the dielectric spectra caused by waters dielectric response (at its various concentration) in the Cl-water system. It is established that the contribution to dielectric properties of zeolite water connected in the zeolite pores and waters in free volume is distinguished. It is shown that the humidity which is less than 12 percent all the water is in a bound state. In Ref. [10] it is established that the modification of some ions increase the dielectric permittivity with respect to the original sample while others reduces. In Ref. [11], the dielectric spectra of natural Cl were measured in vacuum (0.1 Torr) and in air (at atmospheric pressure). Measurements were performed on samples of high density (natural plate) and low density (unpressed-powder). It is established that the frequency dependence of both real and imaginary parts of the dielectric permittivity is characterized by approximately the same dielectric response of about 10^{-5} s. It is concluded that in all these cases, the dielectric spectra are determined by fluctuations of alkali-metal ions associated with the water molecules inside the zeolite pores. A difference in the corresponding dielectric spectra is related to the concentration of these complexes.

The study of the electrical properties was conducted mainly in an alternating electric field. This is due to the fact that the conductivity of zeolites is associated with the movement of ions in the zeolite pores. Previous works were devoted to ionic conductivity of zeolites was assumed that the hydration leads to a weakening of the electrostatic interaction of cations with the framework and, correspondingly, to decrease the barriers to their migration. The ability of the cations to diffuse through the large open zeolite structure gives the possibility of obtaining high ionic conductivity in zeolites. In recent years, there have been many attempts to investigate the possibility of management by ion transport in the external electric field. They are considered in the Ref. [12]. Electrical conductivity of zeolites at an alternating voltage is caused by the movement of positive metal ions in porous framework, and it essentially depends on the content of water in the pores. This explanation is quite suitable for alternating currents. There are not enough studies on the electrical conductivity of zeolites in a constant voltage mode. In Refs. [13–15] the zeolite plate which has been cut from a monoblock natural Cl, on micromonocrystal synthesized zeolites and on the pellets compressed from powder of NZ, respectively. At research of currents at a constant voltage the steady-state current that is not specific for ionic conductivity of the zeolites or continuously decreasing current with time are observed. Therefore controversial question is about possibility the ionic conductivity of zeolites at dc current.

Recently, there is a considerable interest to studying electric properties of zeolitic powders, films and film composites in a constant electric field [16–19]. The electrical conductivity of the zeolite film exhibits ideally two modes: firstly, at low voltages, when the film acts as an insulator and the secondly after the breakdown voltage when the conductivity increases dramatically. Investigation of composite materials based on the zeolite powder is limited by problems of implementing components of a composite into the pores of the zeolite [20]. One of the attractive components for creating composite with zeolite powder is silicon particles coated with natural silicon dioxide SiO₂. The silicon dioxide which is formed on the surface of silicon is an effective absorber of water vapors [20,21].

In Ref. [22] authors studied the electrical properties of the mixture of zeolite and Si powders. The peculiarity of such composite is that both zeolite and particles of Si powder (covered by dioxide of Si) are effective absorbers of water vapors and zeolite particles do not possess electronic conductivity as opposed to particles of low-ohmic Si. It turned out that a small (9%) supplement of the Si particles to the Cl-powder leads to a substantial change in the electrical conductivity of the zeolite powder. Instead of the continuously decreasing current with time, which is typical for ionic conductivity, the steady-state current is observed at constant voltage. At the same time, at a certain feeding voltage (which depends on the air pressure) the current starts to rise sharply with increasing voltage. Considering availability of such strong effect of Si on character of the steady-state current in zeolite powder and assuming possible interaction in such system between the ions, leaving zeolite pores, with Si particles at its various concentrations, we decided to investigate the conductivity at alternating current in a mixture of Cl-powder and Si with different concentration.

Download English Version:

https://daneshyari.com/en/article/1552708

Download Persian Version:

https://daneshyari.com/article/1552708

Daneshyari.com